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A critique of "Brine migration in salt and its implications
in the geologic disposal of nuclear waste," Oak Ridge
National Laboratory Report 5818, by G.H. Jenks and
H.C. Claiborne

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Contents

Introduction.....	1
The water content to be used in the calculation.....	2
Bedded salt.....	2
Conclusions concerning water content of bedded salt.....	7
Domal salt.....	7
Conclusions concerning water content of domal salt.....	8
The rate of migration of fluid inclusions through single salt crystals.....	8
Theoretical equations for liquid brine migration within crystals of NaCl.....	8
Difficulties encountered in the application of the model of Anthony and Cline.....	11
Maximum migration rate as a function of σ in the model of Anthony and Cline.....	14
The effects of brine composition, α , and D on the maximum theoretical migration rate of brine inclusions in single crystal NaCl.....	15
Experimental migration data for liquid brine inclusions in single crystal NaCl.....	15
Kinetic potential.....	20
Significance of the possibility of a threshold value for the temperature gradient, below which no migration occurs.....	20
Conclusions concerning the rate of migration of fluid inclusions through single salt crystals.....	21
The behavior of migrating fluid inclusions when they intersect a grain boundary.....	21
Introduction.....	21
Intergranular water.....	21
"Stopping" of migrating fluid inclusions on intersecting a grain boundary.....	22
Movement of fluid along grain boundaries.....	24
Permeability of salt deposits.....	25
Conclusions concerning behavior of fluid on grain boundaries.....	26
Overall conclusions.....	26
References.....	28
Figures.....	13,16,17,18
Tables.....	12,14

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ABSTRACT

Jenks and Claiborne in 1981 published a 164 page "...comprehensive review and analysis of available information relating to brine migration in salt surrounding radioactive waste in a salt repository." Calculations are presented in that publication, that are called "reasonably conservative," to show that the rates and total volumes of brine expected to migrate into a given emplacement hole in bedded salt over the first 100 years are sufficiently low (e.g., <250 ml/year) that they are of relatively minor concern in the engineering design of a nuclear waste repository. We believe that because the values used for the major input parameters are either nonconservative, selected numbers, or are based on inadequate data, the results of these calculations are invalid. Neither we nor others are able to make a truly valid calculation at this time as there are too many uncertainties, but we show that conservative estimates should be larger, and perhaps two orders of magnitude larger, than those made by Jenks and Claiborne.

INTRODUCTION

One of the factors in establishing the safety, cost, and engineering complexity of any proposed nuclear waste repository in salt centers on the possible migration of brine from the salt into the immediate vicinity of the waste package. Jenks and Claiborne (1981; hereafter abbreviated J-C) have presented a "comprehensive review and analysis of available information relating to brine migration in salt surrounding radioactive waste in a salt repository." The major conclusion of this report, for most potential users, lies in the very low (and hence readily manageable) values that they calculate for the possible rate of inflow of water into a canister chamber (<250 ml/yr.). Although some caveats are mentioned in their report, this value (stated to be "reasonably conservative"), will obviously be used in discussions of the feasibility of such repositories.

This low value is based, however, on a series of assumptions and choices of data from the literature, many of which we show are invalid to some degree, and which taken together have the net effect of greatly reducing the calculated rate of inflow, thus making the result far from "conservative." The most important of these assumptions and choices pertain to: 1) the water content to be used in the calculations; 2) the rate of migration of fluid inclusions through single salt crystals; and 3) the behavior of migrating fluid inclusions when they intersect a grain boundary. Although we take similar issue with numerous other points made by J-C, and have so informed them in the past, the following critique centers on the nature and validity of the assumptions in these three key areas.

It is not now possible to calculate the expected rate of inflow with any confidence, as there are far too many uncertainties and unknowns.

However, we show that a truly conservative estimate of brine inflow should be much higher than that given by J-C, perhaps by two orders of magnitude.

THE WATER CONTENT TO BE USED IN THE CALCULATION

Bedded salt.

Geological and geochemical data are commonly subject to numerous caveats, limitations, and reservations. J-C present a summary of data on the water content of bedded salt deposits and mention (Summary, p. 113) that "The probable maximum amount of liquid water initially present is <0.5 wt%," (emphasis added). They then use a value of 0.5 vol.% brine in their "reasonably conservative" computer calculations by MIGRAIN code of brine migration into a model waste package chamber. This vol.% of brine, if we assume a density of $1.3 \text{ g}\cdot\text{cm}^{-3}$ and a concentration of 35 wt.% salts, in pure halite, is equivalent to 0.19 wt.% H₂O in the salt.

According to J-C, their selection of a water content value is based on the following references: 1) Powers et al. (1978) Chapter 1, Executive Summary (J-C, p. 8)(WIPP); 2) Kopp and Combs (1975) (J-C, p. 10) (WIPP and Project Salt Vault); 3) Beane and Popp (1975) (J-C, p. 10) (WIPP); and 4) Bradshaw and McClain (1971) (J-C, p. 10) (Project Salt Vault).

The reference to Powers et al. (1978) is perhaps the most important. J-C (p. 9) quote Powers et al. (1978) as follows: "Amounts and composition of volatile constituents were determined...Except for samples rich in hydrous minerals (polyhalites, clay partings, potash zones), the vast majority of rock salt contains less than 0.5 weight percent total volatiles." Except for a trivial detail, this is a correct quote from Powers et al. (1978), Executive Summary, p. 1-28.

After this quotation, J-C (p. 10), in their only acknowledgement that any doubts exist concerning the validity of the numbers they use for water in salt, state as follows (modified only to insert in brackets the references in the format used here):

"Roedder and Bassett [1981] have recently reported considerations of possible sources of error in analyses for a specific form of water in rock salt. They concluded that most determinations made in the past are seriously low. However, we see no reasons to question the statement of Powers et al. [1978] with respect to maximum values for the total amount of H₂O within samples of repository-level rock salt at the proposed WIPP site in SENM (see quotation above). Note that the quoted statement excludes samples rich in hydrous minerals (polyhalites, clay partings, potash zones) which could contribute significantly to the total amount of H₂O within a sample. Similarly, we see no reason to question the reported maximum values for the total amount of H₂O within salt in experimental Rooms 1 and 4 of the Project Salt Vault experiment in the Carey Mine at Lyons, Kansas [Bradshaw and McClain, 1971]. The analyses made as part of the Project Salt Vault experiment showed an average of ~0.25 wt %

H₂O. Hydrous minerals occur as impurities at certain levels in both salt formations, but these levels would be avoided in a high-level waste repository."

Let us now look at the nature of the evidence from these four cited references. First, we note that the crucial statement from the Executive Summary of Powers et al. (1978) is not supported by the "vast majority" of the data given in the text of that same report. Thus Table 7.12 of Powers et al., which gives the raw data for one series of analyses of samples from ERDA core 9, lists 34 samples analyzed, of which 15 have more than 0.5% weight loss, and the average is 1.23% weight loss. J-C also state (p. 10) "Note that the quoted statement excludes samples rich in hydrous minerals...", so let us average only those 16 samples that are listed as "major" halite and at most a "trace" of one or two impurities (Powers et al., 1978, Table 7.1). The average of these 16 is 0.72% weight loss. One of these 16, the sample from 2542.0 ft, is listed in Table 7.12 as having 6.39% weight loss, even though this sample is shown to have a very low leach residue (Table 7.6) and to be "rock salt" (Table 7.4). Even if we assume that this number is in error and exclude it (and it need not be wrong, as NaCl with such amounts of inclusion fluid does exist), the average of the remaining 15 is still 0.34 wt.%, which is 79% larger than the 0.19 wt.% H₂O that J-C actually use.

But how were the values quoted from Table 7.12 actually obtained? "Nuggets" were chiseled from the center of the as-received salt core specimens, and ground to a powder a maximum of 10 minutes before weighing of a sample for the thermogravimetric analysis. (This work is presumably that of Beane and Popp (1975), although there seems to be some confusion in the acknowledgements of the sources of data for Chapter 7 (p. 7-109).)

Kopp and Fallis (1973) and Kopp and Combs (1975) reported many determinations on bedded salt from Kansas and New Mexico, based on weight loss after 2-42 days of drying of 1.5- to 2-g samples. They used only the -60, +120 mesh (0.25-0.125mm) fraction screened from the crushed samples, with the rationale that "the size range chosen was small enough to permit rapid dehydration at $102 \pm 3^\circ\text{C}$ while not so small to permit the escape of most of the fluid in inclusions nor to have such a high surface area as to absorb large quantities of atmospheric moisture" (Kopp and Fallis, 1973, p. 8). However, more than 90% of the inclusion fluid in these beds (up to 1.7 wt.% total) is present as inclusions >1 mm in diameter (Roedder and Belkin, 1979a), more than four times the diameter of the largest grains run by Kopp and Combs (1975). Kopp and Fallis (1973, p. 14) indicate that fluid inclusions were actually opened in their crushing operation, as some crushed, whole-rock samples exposed to ambient air (relative humidity range $50 \pm 10\%$) for periods as long as 48 hours lost as much as 1.7 wt.%. Vapor-pressure data on the systems H₂O and NaCl-H₂O (Washburn, 1928) show that pure solid NaCl will absorb water from air with $>75\%$ relative humidity and conversely, will lose all adsorbed water at lower humidities. However, hygroscopic minerals or inclusion bitters containing other salts than just NaCl might well adsorb water under conditions where the fluid from simple saturated NaCl brine inclusions would evaporate completely, and may require high temperatures to boil to dryness (Clynne and others, 1980).

The studies of Kopp and colleagues were on samples that were "similar" (but not aliquots) of those run by Beane and Popp, so the results of the several studies are not directly comparable, and the gross differences found for individual samples are not easily assignable to either laboratory procedures or to real sample variations.

From the above it would seem evident that at least some of the water present as inclusions in the samples as received may not have been present in the samples analyzed. Prof. Kopp (1982) has stated the following:

"The results of our studies revealed that solid, apparently dry mineral matter is capable of releasing large amounts of water if heated even to temperatures well below 200°C. It is probable, on the basis of the studies of Roedder and Bassett (1981), that even larger amounts of water may be released, especially from the rock salt. The procedures we used had some important limitations. The results we reported refer only to the analytical conditions described above (there were no facilities for monitoring fluids released during the crushing of samples, no heating stage microscope for observing the behavior of fluid inclusions during heating, and so forth). The only conclusion we were able to make concerning rock salt was that samples that appeared to be free from visible gypsum, polyhalite, clays, and so forth, typically yielded weight-loss values less than 2 wt % (keeping in mind, under the analytical conditions used)." (Emphasis in original.)

Other data on ERDA core 9, also given in the text of Powers et al. (1978), present a very different picture than that given in their Executive Summary, one that indicates considerably more water may have been present in this salt. Powers et al. (1978) present 51 pages of material (their pages 7-47 through 7-70, plus Tables 7-13 through 7-18 and 20 pages of figures), the great bulk of which is copied (almost) directly from two reports by Roedder and Belkin (1977, 1978). The following four quotations from Powers et al. (1978) are from this copied material (emphasis in original):

P. 7-56--"Table 7.13 shows that these samples now contain a total of from 0.17 to 2.86% fluid by volume, and average 0.61. These values correspond to 0.1 to 1.7 weight percent fluid as extremes, and average 0.36 weight percent. These results are compatible with those reported in Sections 7.5.2 and 7.5.3."

P. 7-56--"Even more important to consider is the bias inherent in these measurements due to substantial and unpreventable loss of inclusions. Examination of the cores showed some centimeter-sized cavities, the sites of former fluid inclusions. No inclusion this size could possibly be included in our count since the plates counted had to be <1 cm in thickness to be translucent. In addition, in situ all natural intergranular porosity in these salt beds was possibly ['presumably' in original] full of fluids. The type D inclusions found represent probably only a trivial part of the total in situ water content present as such imperfectly sealed fluid inclusion[s]. Large

scale in situ porosity tests would be needed to evaluate this variable."

P. 7-62--"Although the salt beds now appear dry to the eye, the samples contain 0.1 to 1.7 weight % fluid as examined, and may contain more in situ."

P. 7-64--"Nuclear Waste Disposal Significance. The most significant aspects at this stage in the study are as follows: First, the amount of fluid water solution now present in the samples as fluid inclusions averages 0.36 weight percent."

Unfortunately, however, even these "quotations" by Powers et al. (1978), while technically correct, have omitted some important qualifications that were present in the original texts, and hence are misleading.

The last sentence of the first "quotation" above, concerning "compatibility," was added by Powers et al., in the editing process but is incorrect in implication as well as in fact. The data reported in sections 7.5.2 and 7.5.3 were obtained by Beane, Kopp, and colleagues, on samples of which over half contained "major" amounts of anhydrite or polyhalite (Table 7.2). Those run by Roedder and Belkin (1977, 1978) were not only essentially pure halite, but were "selected to concentrate work on the horizons of maximum interest" (Roedder and Belkin, 1978, p. 1). They contained 0.005 to a maximum of 0.3 wt.% water-insoluble residue (Roedder and Belkin, 1977, p. 14). Thus the impurity-rich beds that were analyzed by the other workers listed by Powers et al. (1978), and which gave them most of the higher H₂O values they found (i.e., similar to the values Roedder and Belkin found in the pure samples), were not run by Roedder and Belkin.

The following actual quotations should be compared with the "quotations" given above from Powers et al. (1978) (emphasis in original):

Roedder and Belkin (1977, Abstract, p. 1-2): "The total weight % of liquid as fluid inclusions in these 10 samples, as measured, ranged from 0.1 to 1.7%, mostly as type B inclusions; the amount of liquid in these same samples in situ was larger, almost certainly at least twice as large, since many of the largest inclusions, that are the major contributors to the total percentage, and the intergranular fluids, have been drained during the boring and sample preparation."

Roedder and Belkin (1977, p. 15): "Nuclear waste disposal significance The most significant aspects at this stage in the study are as follows: First, the amount of fluid water solution now present in the samples as fluid inclusions averages 0.36 weight percent. The total fluid water present in the beds in situ will be well above this, as each of a series of known factors can only result in a higher true in situ water content. This could have major physical and chemical effects."

Roedder and Belkin (1978, p. 11): "Although the salt beds now appear dry to the eye, the samples contain 0.1 to 1.7 weight % fluid as examined, and may contain double these amounts in situ."

Roedder and Belkin (1978, p. 13): "Amount of water in the beds. Although this is the most important single datum that might be obtained from inclusion studies, we can only provide minimum values. The nature of the samples and the necessary sample preparation are such that there is a bias toward low values built in to these data. Thus the 0.1 to 1.7 weight percent fluid actually found in these individual samples may represent perhaps only half (or even less) of the liquid that was present in these beds in the ground before sampling."

J-C also refer to the work of Bradshaw and McClain (1971) at Project Salt Vault, in Kansas, for support for their assumption as to water content. Bradshaw and McClain (1971) heated "1-2 pound chunk" samples of bedded salt from Kansas to 400°C for unspecified times and weighed the total water evolved. At such temperatures, most hydrous minerals should have dehydrated, and most fluid inclusions should have decrepitated. Such high temperature dehydrations, if maintained for enough time, probably yield the total water values of the samples used. Roedder and Bassett (1981) have shown, however, that if clay or silt is present in the rock salt cores, long heating times may be necessary for dehydration at the temperatures normally used. For example, one 255-g segment of silt-bearing bedded rock salt core from the Palo Duro basin, Texas, showed continued weight losses that were almost perfectly linear with time, even after 232 hours in vacuum at 300-352°C. Even small samples of powdered material from this core take over 1 1/2 hours to reach equilibrium weight loss, both at 35°C and at 350°C.

Bradshaw and McClain (1971, p. 5-6 and 170) obtained 0.048 to 0.293 wt.% H₂O from 8 samples of salt from Hutchinson and Lyons, Kansas, and a value of 1.08 wt.% for a sample of "clear crystal, atypical." (At the WIPP site, Roedder and Belkin, 1977 and 1978, report that the largest fluid inclusions are usually present in just such clear halite crystals, and yielded the highest water values found for any salt sample studied from the two proposed emplacement horizons.)

Bradshaw and McClain (1971, p. 170) also examined the water content of core samples obtained from near the test after the Project Salt Vault heating was terminated. Water was determined by heating the samples (of unspecified size) to 625°C (for unspecified times). The averaged water content was "about 0.50%" (the units are unstated, but are here presumed to be volume percent).

Roedder and Belkin (1981) have shown that much of the fluid inclusion liquid in salt beds can be lost as a result of surface fracturing during coring operations, and Roedder and Bassett (1981) have shown that loss of intergranular fluid inclusions that have been opened at the core surface can be significant even in 4" diameter core. Furthermore, they show that unless great care is exercised, core samples will lose further intergranular water in storage, yielding the familiar white incrustations outlining grain boundaries on the core surface.

Conclusions concerning water content of bedded salt.

From the above it is evident that the data and conclusions of Roedder and Belkin (1977 and 1978) on the water content from fluid inclusions alone (not including water in clays, polyhalite, etc.) have, in effect, been minimized in the text of Powers et al. (1978). These "minimized" data have subsequently been ignored in the writing of the Executive Summary of that same report, where "less than 0.5 weight percent total volatiles" is given as established fact. J-C quote these same 0.5 wt.% data in their text, but then use 0.5 volume% (= 0.19 wt.% H₂O) for the total water content in their "reasonably conservative" calculations. By this means they show that brine migration into a canister chamber is expected to be only 250 ml/y (or 180 ml/y^{1/}) which all would agree is apt to be an inconsequential amount. However, calculations based on the water data reported by Roedder and Belkin (1977, 1978) would yield larger brine migration values. Thus the average inclusion content reported by them (0.36 wt.%) is a factor of 2 higher, and the maximum found (1.7 wt.%) is a factor of 9 higher. But these data are for intracrystalline liquid inclusions only. They do not include hydrous minerals, or intergranular fluids, which Roedder and Belkin indicate would "almost certainly" double these figures again.

Domal salt.

In their Summary and Conclusions (p. 117) J-C state "The maximum amounts of liquid H₂O initially present in domal salts are probably <0.2 wt.%" but then in their Executive Summary (p. xxi) they assume 0.03 wt.% liquid water present as brine, and using this figure, calculate inflows of water into a canister chamber of 25 ml/year or less. In their Abstract (p. 2) they indicate that these calculated rates and total amounts of in-migration are "very conservative for domal salts..." Their basis for their assumption of 0.03 wt.% lies in the following references (their pages 12-14): Jenks (1980); Kaufman (1960); Knauth and Kumar (1981); Martinez et al. (1978, 1979); and Roedder and Belkin (1979b).

As there is almost a continuum from horizontally bedded salt through various degrees of deformation into salt anticlines and diapirs to standard salt domes, it is difficult to draw a dividing line between "bedded" and "domal" salt. Most geologists would include salt anticlines, with their steep dips and evidence of considerable salt flowage (such as Asse, W. Germany), in the "domal" category.

Knauth and Kumar (1981) report analyses of total water in salt from six salt domes in Louisiana, in which 3- to 56-g samples were completely vaporized by heating to 1000°C in vacuum. The evolved water was converted to hydrogen and measured manometrically, resulting in very high sensitivity. Most of the samples evolved <0.02% H₂O and some single crystals evolved

^{1/} The maximum inflow stated in the Abstract of only "~180 ml/y," rather than the "250 ml/y" given in the Executive Summary, and the Summary and Conclusions, comes about by an assumption of a lower thermal loading as mentioned on p. 97.

only 0.0001% (i.e., 1 ppm). Water evolved above 220°C was shown to be free from surface contamination. The ranges (in wt.% H₂O) for the data from these six domes were as follows (number of samples run in parentheses): Weeks Island (10) 0.01-0.09; Belle Island (6) 0.003-0.52; Jefferson Island (4) 0.001-0.004; Avery Island (3) 0.003-0.004; Vacherie (5) 0.001-0.004; Rayburn (5) 0.0005-0.006. Samples from the first four domes were mine samples; the last two are from cores. The lowest value, from Rayburn dome, was from a halite single crystal. The high values are from "anomalous" (i.e., relatively wet) zones. The only question in this work is whether these samples can be considered valid, representative samples of a volume of salt adequate to be considered for a repository. As shown by Martinez et al. (1978, 1979, 1980), many Louisiana salt domes have shear zones, inclusions of other sedimentary rock, and "wet zones," and similar observations have been made at many other salt domes.

Roedder and Belkin (1979b) reported that the amount of fluid visible as fluid inclusions (i.e., not including any water present in other forms) in 18 core samples from the Rayburn and Vacherie domes was "...small, certainly <0.1 vol.% and probably in the range 0.01 to 0.001 vol.%, but the inclusions are highly erratic in distribution."

Other water data, on other domes, are considerably higher. Kaufman (1960) reports an average of 0.022 for 7 analyses of salt from Avery Island, and J-C (p. 76) report ~0.2 wt.% H₂O for core samples from the brine migration test site at Avery Island. Hite et al. (1979) reported an average of 0.21 wt.% H₂O using Karl Fischer titration on 1-kg samples from a non-diapiric salt anticline, Northern Paradox Basin, Utah. In a 1981 personal communication, R.J. Hite reports these preliminary values may be anomalously high, but that 22 samples of very pure salt from a diapiric salt anticline in Salt Valley, Utah, yielded a range of 0.008 to 0.117 wt.% H₂O. Jockwer (1979, 1980, 1981, and personal communications) reported analyses of 48 samples from the Asse salt anticline, FRG, made by four different methods (see particularly, Jockwer, 1981, p. 36). Only three of the 48 samples show <0.01% H₂O by any of the methods used. A total of about 30% of the analyses show >0.1% H₂O. The average amount found for samples from the areas of interest for nuclear waste disposal (Jockwer, 1979, 1980) is about 0.15 wt.%.

Conclusions concerning water content of domal salt.

The total amount of water present in domal salts will obviously average well under that from bedded salts, and hence the brine migration problems will be much less. But we believe that the data above show that a value higher than 0.03 wt.% (e.g., 0.1%) would be more appropriate to use as the basis for a "very conservative" calculation of the possible brine inflow into a canister chamber from such salt.

THE RATE OF MIGRATION OF FLUID INCLUSIONS THROUGH SINGLE SALT CRYSTALS

Theoretical equations for liquid brine migration within crystals of NaCl

The theory concerning the migration of all-liquid inclusions in salt crystals induced by a thermal gradient was reviewed by J-C. They concluded

that the equation of Anthony and Cline (1971) and a modified version of an equation of Geguzin (Olander et al., 1980, 1982a) are equivalent. They also stated (p. 15-16) that

"Some incorrect theoretical equations for brine migration rates that were reported prior to the work of Anthony and Cline are described in Appendices A and E, where it is also demonstrated that these equations are in agreement with Anthony and Cline when their errors are corrected."

The models of Wilcox (1968) and Hoekstra et al. (1965) were reviewed in their Appendices A and E, respectively. We do not have any problem concerning the derivation of the theoretical equations of Anthony and Cline given by J-C. However, we do not think that the models of Wilcox and Hoekstra et al. are in error. The model of Anthony and Cline was derived from a thermodynamic approach while those of Wilcox and Hoekstra et al. were from mass balance considerations. J-C (p. 147) recognized that

"The straightforward mass balance approach that considers on [sic.] the liquid domain (as exemplified in Appendixes A and C) and then folds in the irreversible effects as shown in Sect. 3.1.5, also seems correct within the assumptions made and possesses the advantage that boundary conditions can be applied exactly."

The errors indicated by J-C in the models of Wilcox and Hoekstra et al. are actually a result of misinterpretations made by J-C.

In the model of Wilcox, the equation for the rate of movement of an inclusion is

$$V = \frac{D \nabla T_{\ell} \rho_{\ell}}{m(1-w_{\ell p}) \rho_s} \quad (1)$$

(Eq. A-12 in Appendix A of J-C). J-C mistakenly claimed that the above equation can be replaced by

$$V = \frac{\nabla T_{\ell} D (\partial C_E / \partial T)}{(C_s - C_{\ell})} \quad (2)$$

(Eq. A-13 in Appendix A of J-C). In fact, the above equation is exactly the equation derived from the model of Nernst (Eq. (1) of Cheung et al. (1980)), and is not the same as eq. (1). Some additional minor mistakes in Appendix A of J-C are

- (a) Eq. (A-6) should read $LV\rho_s/D\rho_{\ell} \ll 1$;
- (b) The subscript ℓd for w in eqs. (A-7) and (A-8) should be eliminated;
- (c) The "D" in the $LD\nabla T_{\ell}$ term in eq. (A-11) should be eliminated.

In Appendix E of J-C, the model of HOWS (i.e., the model for movement of liquid inclusions in ice derived by Hoekstra et al. (1965) and modified by Seidensticker (1966)) was summarized by their eq. (E4)

$$V = - \frac{D}{C_\ell} \left(\frac{\rho_\ell}{\rho_S} \right) \left(\frac{\partial C_E}{\partial T} \right) \nabla T_\ell \quad (3)$$

J-C (p. 150) indicated that ρ_ℓ/ρ_S in the above equation was defined by Seidensticker (1966) as

"the ratio of the molecular volume of the solid to that of the liquid (he undoubtedly meant the ratio of the liquid to the solid). He did not mention the conceptual error that water, rather than salt, is the diffusing component in the model. However, it was tacitly recognized, since he used $\rho_\ell/\rho_S = 1.08$, which is the ratio of the molar density (or mass density) of water and ice."

The above statement by J-C is quite different from the following statement made by Seidensticker (1966):

"Since the velocity measurements were made with respect to the solid, the correction factor is the ratio of the molecular volume of the solid to that of the liquid. Again, the latter parameter is relatively insensitive to the presence of solute, and the density ratio of the pure phases may be used, giving $\rho_\ell/\rho_S = 1.08$."

The important points are:

(a) The correction factor (defined as k from here on) is the ratio of the molecular volume of the solid to that of liquid, (not the ratio of the liquid to the solid stated by J-C).

(b) The equation derived in the model of HOWS should read

$$V = \frac{Dk}{C_\ell} \left(\frac{\partial C_E}{\partial T} \right) \nabla T_\ell \quad (4)$$

For the migration of liquid inclusions in single ice crystals, k is relatively insensitive to the presence of solute, and the density ratio of the pure phases may be used, giving

$$k \approx \rho_\ell/\rho_S = 1.08 \quad (5)$$

However, if this model is applied to calculate the migration rate of brine inclusions in single salt crystals, the approximation in eq. (5) is no longer true, and should be replaced by the equation

$$k = f \rho_\ell/\rho_S \quad (6)$$

which is still "the ratio of the molecular volume of the solid to that of the liquid" as defined by Seidensticker (1966).

(c) Nothing is wrong in the model of HOWS. The numerical values derived from eqs. (4) and (6) for the migration rates of brine in single salt crystals are exactly the same as those derived from the model of Anthony and Cline (1971) when velocities due to thermal diffusion (Soret effect) and kinetics at interface in the later model are ignored. The erroneous uses of the model of HOWS by Bradshaw and Sanchez (1968 and 1969), and by Cheung et al. (1980) do not affect the validity of the model.

Difficulties encountered in the application of the model of Anthony and Cline

We agree with J-C that the model of Anthony and Cline (1971) is the most complete theoretical model available. However, we do not think there are enough experimental data to verify it. To obtain a set of numerical values for the parameters of this migration model, some assumptions and extrapolations are necessary. Unfortunately, some of the numerical values of these parameters chosen by J-C are arbitrary and/or theoretically unsound. Uncertainties associated with these estimated numerical values were not given by J-C. This is not surprising, because in most cases the working models for these numerical estimations are not well established, and there is essentially no way to make the uncertainty estimations; unfortunately, the validity of the results rests on them. Some discussions on the numerical values for three of the migration equation parameters are given here.

(a) The numerical values for C_ℓ and $\frac{1}{C_\ell} \cdot \frac{\partial C_E}{\partial T}$ reported by Jenks (1979) are not correct due to the use of the wrong concentration unit (molal). However, following our suggestions, those numerical values given in the tables on p. 28 and 29 in J-C (1981) for 2.4 m $MgCl_2$ and $NaCl-H_2O$ brines are in the correct concentration unit (molar).

(b) The numerical values for the diffusion coefficient of NaCl in NaCl-saturated solutions, D , listed in the table on p. 29 of J-C are from Olander et al. (1982b). These values are not the same as those given by Jenks (1979). No explanations were given by J-C for their adoption of the data from Olander et al. Experimental data for the diffusion coefficient of NaCl in NaCl-saturated brines are not available. However, the Stokes and Einstein relationship has been widely used to estimate D values at elevated temperatures (Jenks (1979); Cheung et al. (1980); Olander et al. (1980); Bradshaw and McClain (1971)). Unfortunately, for ionic species in water, the Stokes and Einstein relationship is not ordinarily obeyed (Lerman, 1979, fig. 3.2, p. 88), therefore the D values adopted by J-C have no scientific basis. It should be emphasized that there is no working model available at present for estimating the values of D . Following the procedures suggested by R.W. Potter II, (personal communication), Chou (1982)^{1/}, presented high-temperature values for D obtained from various

^{1/} Most of the information contained in this paper was provided to Drs. Jenks and Claiborne in our previous reviews of their paper dated May 12 and August 18, 1981.

equations that fit the diffusion coefficient data given by Washburn (1928) for 0.05 M NaCl solution. Unfortunately, the data in Washburn are restricted to temperatures between 5° and 30°C, and there is no warranty that the fitted equations can be extrapolated to much higher temperatures. Furthermore, the effects of the other cations and anions present in the brine inclusions on the diffusion coefficient of NaCl are not known. The D values presented by Chou (1982) are believed to be more conservative than those of J-C. The effect of the variations in the estimated D values on the migration rate calculations will be discussed later.

(c) Some literature data for the numerical values of the Soret coefficient in NaCl solutions were presented by J-C in their Fig. 5 (p. 31). The numerical values for $(-\sigma)$ estimated by J-C are probably too low. For example, J-C stated (their p. 30) that "the reported experimental values for the Soret coefficient in concentrated NaCl solutions at 30 to 50°C is $\sim 0.002^\circ\text{C}^{-1}$, as illustrated in Fig. 5." However, in their Fig. 5, it is clearly shown that $(-\sigma) = 0.002$ at 33°C and its value increases rapidly with temperature and exceeds 0.003 at 50°C. It should also be noted that we are interested in the average temperature (T_{av}), not the maximum temperature (T_{max}) shown in their Fig. 5. The experimental data compiled by Potter (personal communication, 1979; also provided to Drs. Jenks and Claiborne on May 12, 1981) are given in table 1. The data of Hiby and

Table 1. Summary of the experimental data for σ (Potter, personal communication)

T(°C)	M	$-\sigma \times 10^3$	Source
32	1.00	1.46*	Tanner (1927)
37	1.00	2.48*	Tanner (1927)
55	1.00	5.5	Hiby and Wirtz (1940)
55	0.1	5.4	Hiby and Wirtz (1940)
25	0.01	2.30	Agar (1959)
34.7	0.01	3.28	Agar (1959)
25.3	0.01	2.05**	Snowdon and Turner (1960)
25	0.5	1.00	Chanu (1959)
25	1.0	1.16	Chanu (1959)
25	1.5	1.35	Chanu (1959)
42.5	0.1	3.01	Schott (1973)
42.5	0.5	3.05	Schott (1973)
42.5	1.0	2.98	Schott (1973)

* Data cited by Jenks (1979).

** For a 0.01 molal NaCl solution.

Wirtz (1940) at 55°C were ignored by J-C, who claimed that these data are less reliable and pertinent (their p. 30). However, in a plot of σ vs. T (Fig. 1), it is clear that the data of Hiby and Wirtz (1940) are consistent with the rest of the data for NaCl. It is also clear from that diagram

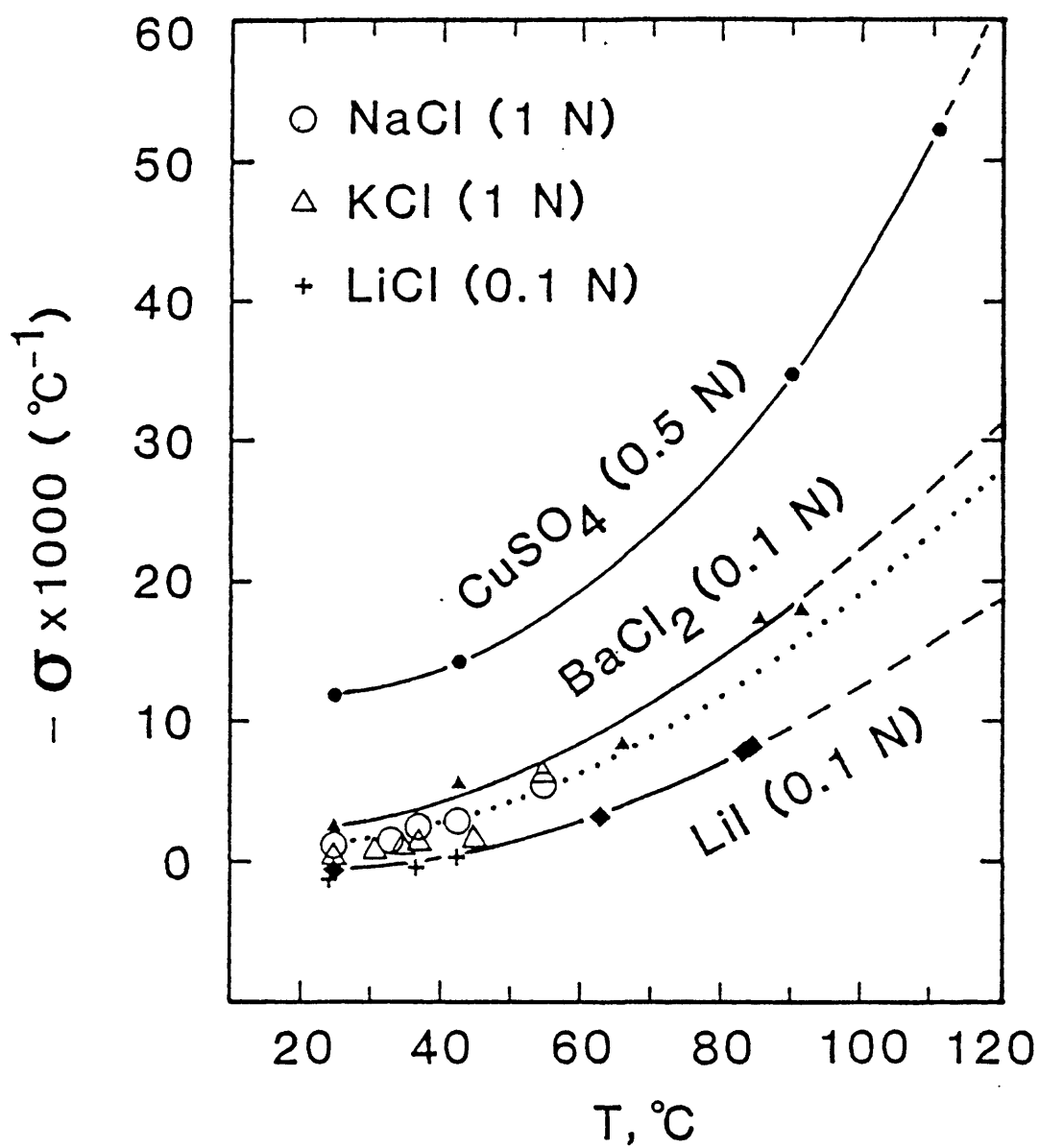


Fig. 1. Soret coefficients of various salts in aqueous solution as a function of temperature. The dotted line represents σ - T relationship in 1N NaCl solution (for detail, see Chou (1982)).

that the σ -T relationship for NaCl tends to follow the general trend of the σ -T relationships for BaCl₂ and LiI and that σ for NaCl is extremely sensitive to temperature. The statement made by J-C (their p. 30-32) that

"However, analyses and correlations of experimental and theoretical information (presented in Sect. 4.1.1) indicated $-\sigma$ values for the natural inclusions in bedded salt vary from 0.004 and 0.005°C⁻¹ in the temperature range 50 to 200°C..."

is scientifically unsound (see p. 19). According to Fig. 1, $(-\sigma)$ for NaCl at 100°C is very likely to exceed 0.015, which is very close to the values estimated by Potter (personal communication; given as table 2 in

Table 2. Extrapolated values of $-\sigma \times 1000(^{\circ}\text{C}^{-1})$ using various functions of $1/T$ (Potter, personal communication)

T(°C)	[1]	[2]	[3]	[4]
25	0.7	1.1	1.1	0.8
50	4.4	4.4	4.4	4.5
100	10.4	18.6	18.3	16.3
150	15.0	36.9	36.0	30.1
200	18.6	55.8	54.2	43.8

[1] Linear $1/T$ function

[2] Second order $1/T$ function

[3] Second order $1/T$ function deleting the 55°C data point

[4] " " " " " " 25°C " "

this paper). The effect of other cations and anions on the σ values has been discussed by Chou (1982).

Maximum migration rate as a function of σ in the model of Anthony and Cline

As recognized by J-C (p. 30) concerning σ values that "No experimental or reliable theoretical values are available for higher temperatures in NaCl solutions or for the MgCl₂ solutions that occur as brine inclusions in bedded salt," it is necessary to calculate the maximum migration rate of brine inclusions in single crystals of NaCl as a function of σ at each temperature (J-C, table 1, p. 33, and table 4, p. 43). However, the presentation of $V_{\max}/V_{T\infty}$ can be simplified by plotting this parameter against σ for each temperature according to the linear relation

$$V_{\max}/V_{T\infty} = a \sigma + b, \quad (7)$$

where $a = -\alpha D C_\ell / C_s$; $b = \alpha D (\partial C_\ell / \partial T) / C_s$; and $\alpha = \nabla T_\ell / \nabla T_\infty$ (Chou, 1982, Figs. 1 and 2; reproduced in this paper as Figs. 2 and 3 respectively). We suggested the above form of presentation to J-C in our previous reviews of their paper, but it was not adopted by J-C, probably because they did not believe that $-\sigma$ values for the natural inclusions in salt may respond to the temperature change as dramatically as described in the previous section.

The effects of brine composition, α , and D on the maximum theoretical migration rate of brine inclusions in single crystal NaCl

From eq. (7), it is clear that the numerical value of $V_{\max} / \nabla T_\infty$ depends on the brine composition (C_ℓ and $\partial C_\ell / \partial T$ are brine-composition dependent) as well as α and D. This dependence was not clearly pointed out by J-C. The effects of brine composition on $V_{\max} / \nabla T_\infty$ are shown in Figs. 2 and 3 for four brine compositions and also indicated by J-C (table 1, p. 33) for two brine compositions. The effects of D and α are shown in Figs. 3 and 4, respectively. From these diagrams, it is clear that the effect on $V_{\max} / \nabla T_\infty$ by changing brine composition and the numerical values of D and α is larger when the assumed ($-\sigma$) values become larger.

Experimental migration data for liquid brine inclusions in single crystal NaCl

The data for bedded salt in the Cary mine, Hutchinson, Kansas, reported by Bradshaw and Sanchez (1968) were summarized by J-C (section 4.1.1, p. 40-42). It should be noted that the data scattered appreciably and that the curve shown in Fig. 6 of J-C, (p. 40) and represented by their equation (42) is just an arbitrary curve assumed by Jenks (1979) to represent the maximum rates indicated by the data. We have compared the results obtained by J-C from the "arbitrary" curve with the other experimental data and the theoretical migration rates in the $V_{\max} / \nabla T_\infty$ vs. σ plots discussed in the previous section (Figs. 2(b), 3(a), and 3(b)). The other experimental data shown in these diagrams include data for bedded salt in SENM (Roedder and Belkin, 1980a; and section 4.1.2 in J-C, p. 42 and 44), and data for bedded salt in the Carey mine at Lyons, Kansas (Shor and Baes, 1978; and section 4.1.3 in J-C, p. 44).

J-C state (p. 42) that:

"Jenks (1979) made comparisons between the experimental values for $V_{\max} / \nabla T_\infty$ shown by Eq. (42) for the temperature range 50 to 200°C, and the theoretical values found using Eq. (1), with $K = 0$. He observed that the experimental and theoretical values were in near agreement for both sets of data when the assumed values for $-\sigma$ were in the range 0.003 to 0.004°C⁻¹ and the assumed values for the other quantities in Eq. (1) were near those described in Sect. 3.1.8.

Table 4 shows a similar comparison made using the revised values for C_ℓ / C_s , $(1/C_\ell)(\partial C_\ell / \partial T)$ and D in Sect. 3.1.8. Near agreement between experimental and theoretical values is

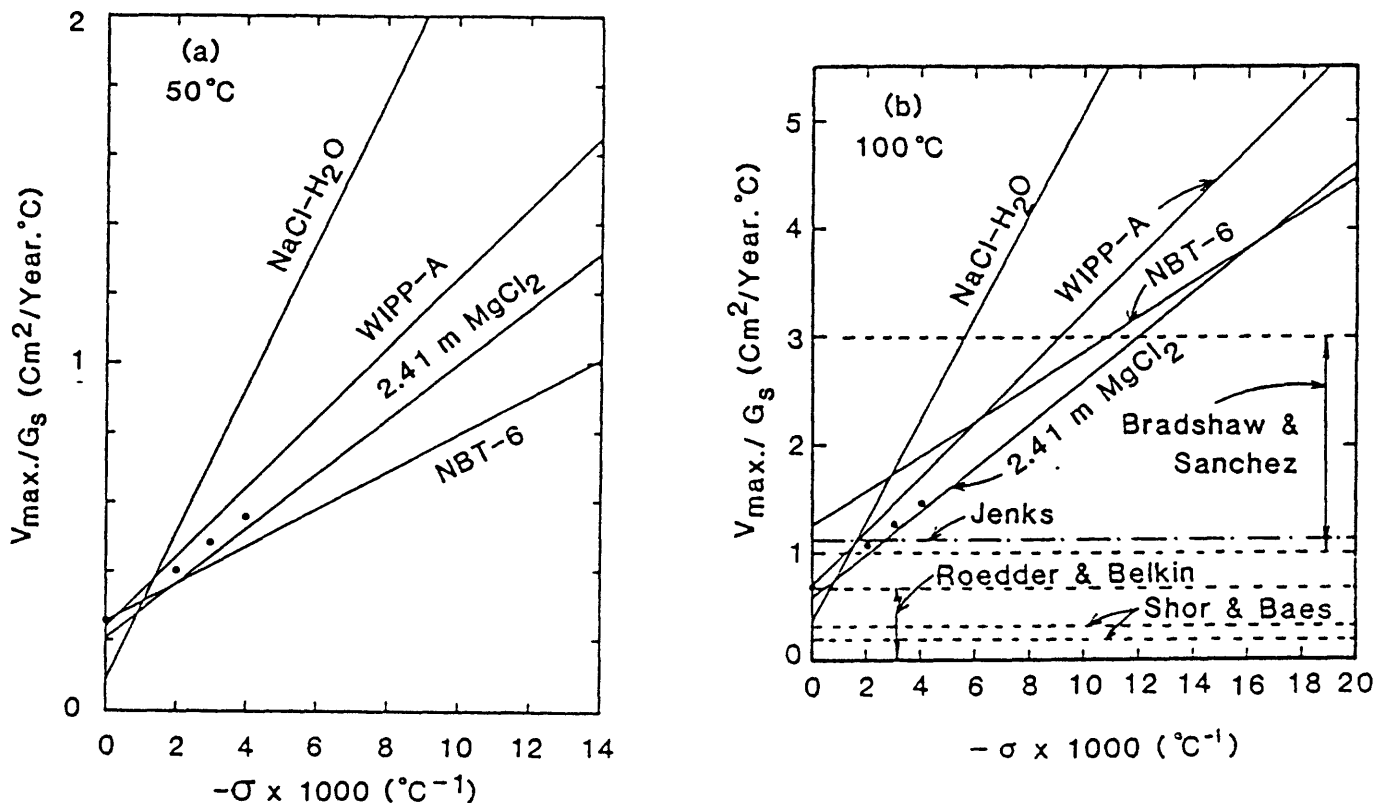


Fig. 2. Maximum migration rates as a function of the Soret coefficient at 50°C (a) and 100°C (b) for halite-saturated NaCl-H₂O, WIPP-A, 2.41m MgCl₂, and NBT-6 brines obtained by using $\alpha = 1.4$ and $D = 3.2 \times 10^{-5}$ (a) and 7.1×10^{-5} (b) cm^2/sec . The filled circles are values given by Jenks (1979) for halite-saturated 2.41m MgCl₂ brine. The horizontal dashed lines in Fig. 2b are experimental data. The data of Roedder and Belkin (1980a) are for 108°C ambient temperature, and the maximum value indicated is for inclusions of $10^9 \mu\text{m}^3$ volume. The two values reported by Shor and Baes (1978) are for inclusions measuring $150 \times 100 \mu\text{m}$ (upper line) and $65 \times 65 \mu\text{m}$ (lower line). The dash-dotted line represents the value assumed by Jenks (1979) as a conservative representation of Bradshaw and Sanchez's (1968) data. Note that $G_s = \nabla T_\infty$. (For detail, see Chou (1982)).

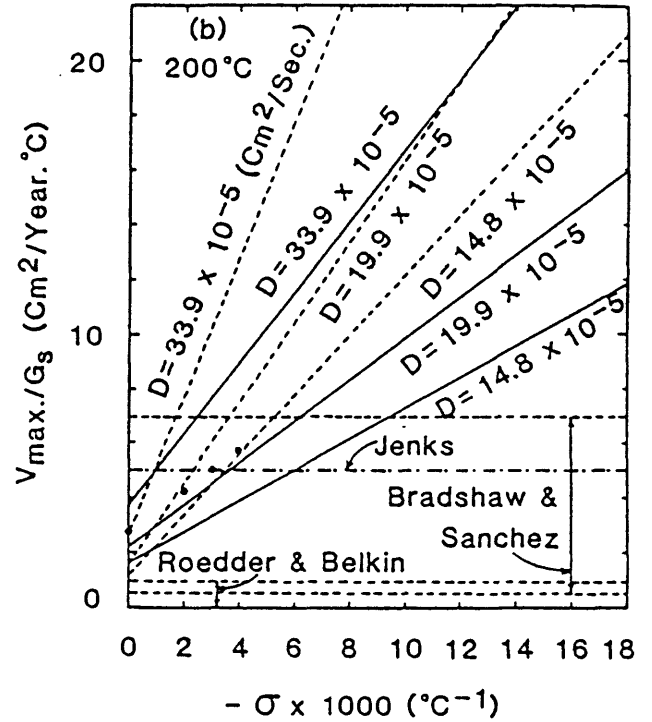
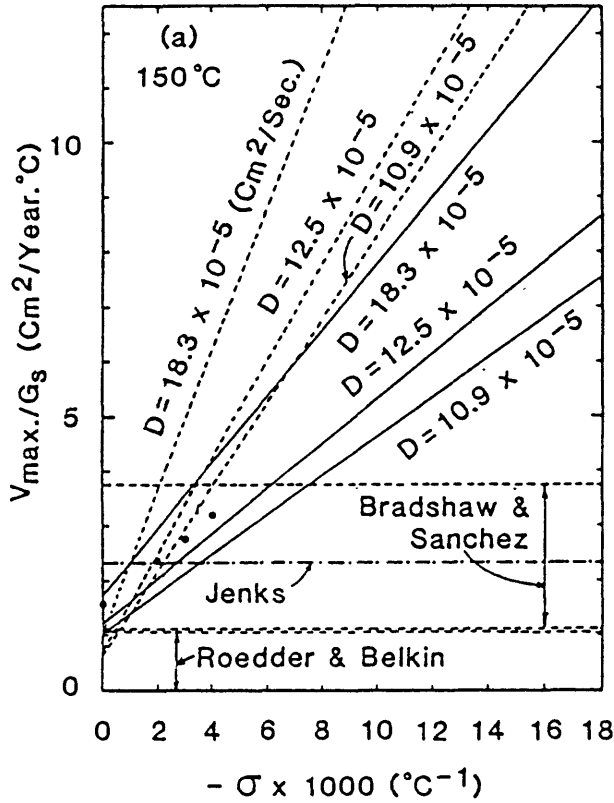


Fig. 3. Maximum migration rates as a function of the Soret coefficient at 150°(a) and 200°C(b) for halite-saturated NaCl-H₂O (oblique dashed lines) and 2.41m MgCl₂ (solid lines) brines obtained by using the maximum, minimum, and Jenks' D values given in Chou (1982, Table II) and $\alpha = 1.4$. The other symbols are the same as in Fig. 2. Data of Roedder and Belkin (1980a) are for 160°(a) and 201°C(b) ambient temperatures. (For detail, see Chou (1982)).

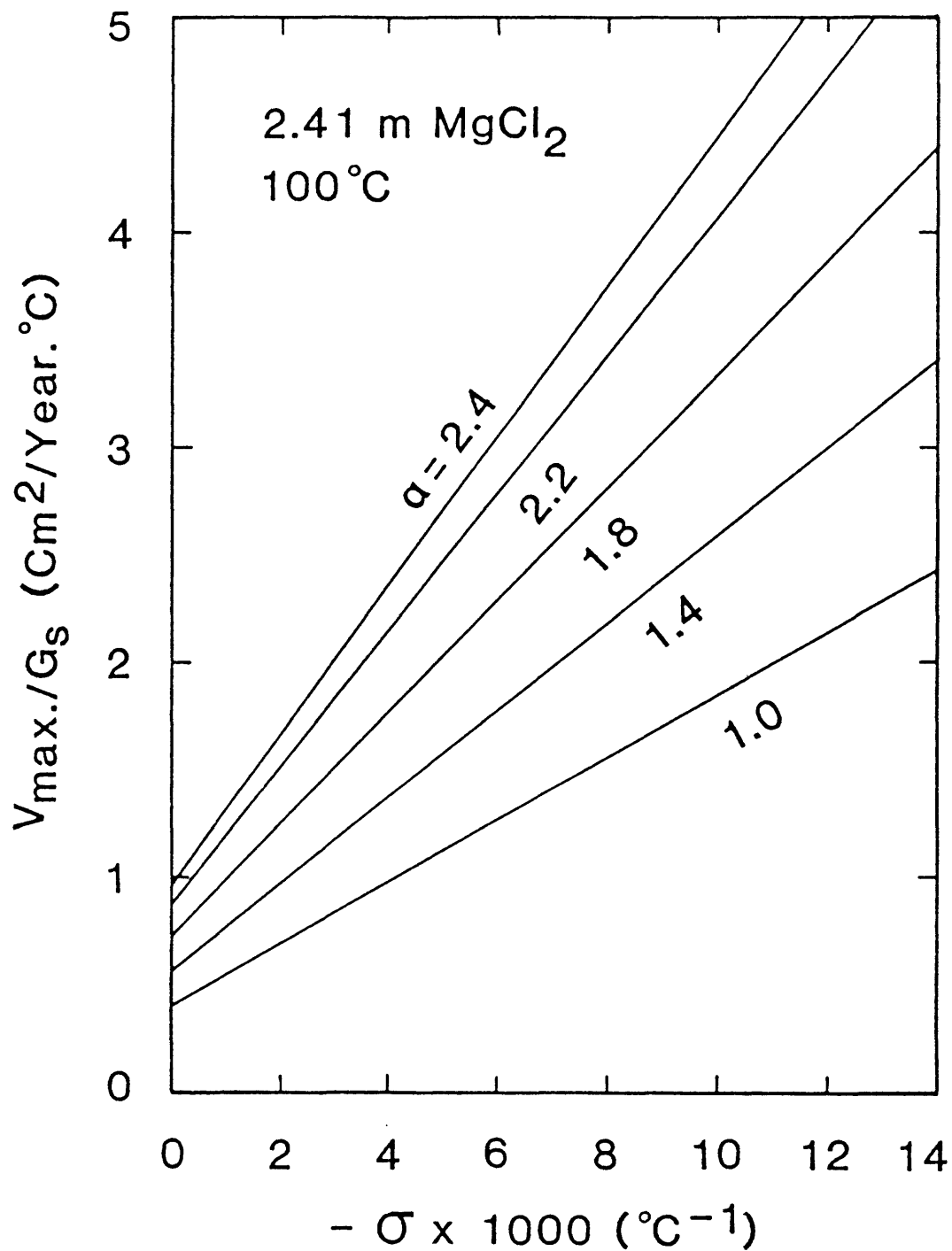


Fig. 4. The effect of aspect ratio, X/L , or the temperature gradient magnification factor, α , on the calculated migration rates for 2.41m MgCl_2 brine inclusions at 100°C. $\alpha = 1.4, 1.8, 2.2$, and 2.4 correspond to $X/L = 1, 2, 3$ and 4 respectively. $\alpha = 1.0$ is the minimum where $G_l (= \nabla T_l) = G_s (= \nabla T_\infty)$. (For detail, see Chou (1982)).

indicated when the values for $-\sigma$ are in the range 0.004 to $0.005^{\circ}\text{C}^{-1}$."

This statement implies that the theoretical curves such as those shown by the solid lines in Figs. 2 and 3 should intersect Jenk's arbitrarily chosen migration rates (shown as horizontal dash-dot lines in Figs. 2 and 3) at $-\sigma$ values between 0.004 and $0.005^{\circ}\text{C}^{-1}$ for the temperature range 50 to 200°C . However, it is scientifically unsound to imply that

"analyses and correlations of experimental and theoretical information (presented in Sect. 4.1.1) indicated $-\sigma$ values for the natural inclusions in bedded salt vary from 0.004 and $0.005^{\circ}\text{C}^{-1}$ in the temperature range 50 to 200°C " (J-C, p. 30-32)

This is because the locations of the theoretical curves shown in these diagrams depend strongly on the numerical values for C_L , $(1/C_L)(\partial C_E/\partial T)$, D , and α used in the calculation, and the migration rates assumed by Jenks are arbitrary. In other words, we don't have much control on the positions of either of two intersecting lines, one theoretical and one experimental. Therefore it is difficult to predict the σ value which is defined by the position of intersection of these two lines, assuming that the model of Anthony and Cline is adequate and that there is no kinetic potential involved in the migration experiment. Whether the model of Anthony and Cline is adequate or not is hard to tell because we don't have enough data to verify the model. However, it is contradictory to accept that there is no kinetic potential involved in the migration experiments of Bradshaw and Sanchez (1968) while claiming there is kinetic potential involved in the experiments performed by Roedder and Belkin (1980a) and Shor and Baes (1978) (J-C, table 5, p. 45).

Even though J-C (p. 39) clearly pointed out that the data of Bradshaw and Sanchez (1968) scattered appreciably, they failed to show the effects of the uncertainties associated with the assumed arbitrary curve (J-C, eq. 42, p. 39). For example, at 150°C (Fig. 3(a)) the $V_{\max}/\nabla T_{\infty}$ derived from the data of Bradshaw and Sanchez (1968) range from 1.1 to 3.7 $\text{cm}^2/\text{year}^{\circ}\text{C}$. In order to match these data with the theoretical migration rate with $D = 10.9 \times 10^{-5}$ cm^2/sec and $\alpha = 1.4$, $-\sigma$ values have to range from 0.0002 to $0.0075^{\circ}\text{C}^{-1}$.

Roedder and Belkin (1980a, Fig. 2, p. 457) demonstrated that the migration rate of brine inclusions in single crystal NaCl is a function of inclusion size. The data of Shor and Baes (1978) are in good agreement with those of Roedder and Belkin when the sizes of the brine inclusions are taken under consideration (Chou, 1982, table VI). The maximum inclusion size studied by Roedder and Belkin (1980a) was $(1\text{mm})^3$, while the inclusions studied by Bradshaw and Sanchez (1969) ranged from 2 to 10 mm on an edge. This might explain why most of the migration rates reported by Bradshaw and Sanchez are substantially higher than those reported by Roedder and Belkin and Shor and Baes. Unfortunately, the relationship between migration rate and inclusion size was not documented by Bradshaw and Sanchez.

Kinetic Potential

The difference between the theoretical maximum migration rate predicted by the model of Anthony and Cline (1971) and the smaller measured migration rate was interpreted by J-C as being due to kinetic potential, K . However, the difference could just as well be due to the deficiencies of the model and/or the use of incorrect numerical values for the parameters in the model.

Instead of presenting values for K , J-C (table 5, p. 45) reported values for β and b , assuming $\sigma = -0.004^\circ\text{C}^{-1}$ and

$$K = \beta V + b. \quad (8)$$

We have shown that $-\sigma = 0.004^\circ\text{C}$ is not reliable and is probably too low. Furthermore, the linear relation given in eq. (8) was demonstrated by Cline and Anthony (1972) only for KCl, at room temperature, for V less than 1 nm/sec. We feel that it is very questionable to simply assume that a linear relation will hold for NaCl solution at temperatures considerably higher than room temperature and at various migration rates. Therefore, we also feel that it is inappropriate to substitute from eq. (8) into the model of Anthony and Cline and obtain the final equation shown as eq. (5) in J-C (p. 19).

To obtain values for K from experimental migration rates, theoretical maximum migration rates (V_{\max}) are required. As shown in Figs. 2 and 3, values for V_{\max} depend on brine composition, in large part because $\partial C_2/\partial T$ for complex brines is greater than that for simple NaCl-H₂O solutions, even though the total solubility of NaCl is lower in the brines. On the other hand, Roedder and Belkin (1980a, p. 460) reported that the experimental migration rate for NaCl-H₂O brine were about the same as the WIPP sample 2061 (presumably NaCl-saturated 2.4 m MgCl₂ brine). What brine composition should be used to calculate V_{\max} , which in turn will be used to calculate K , is a problem. The situation is further complicated by the dependence of V_{\max} on the values of estimated D and α . Therefore, we suggest that the values given by J-C (table 5, p. 45) for β and b are not definitive, and may not even be approximate.

Significance of the possibility of a threshold value for the temperature gradient, below which no migration occurs.

J-C (Executive Summary, p.xx) assumed that a threshold temperature gradient, ∇T_{\min} , exists (below which no migration of inclusions within crystals takes place), and that they can predict this temperature gradient using theoretical and experimental information as discussed in their report (similar assumptions were made by Pigford, 1982). This gradient was calculated from eq. (53) of J-C (p. 98), and subsequently used to provide an estimate of an upper-bound for the salt volume that could contribute to brine in-migration, and therefore the maximum total volumes of in-migration of H₂O (J-C, tables 13-15, p. 100-102). On the basis of several lines of evidence, the validity of this all-important "threshold" gradient is questionable at best: 1) The experimental evidence for such a threshold is based on data from inclusions in KCl at 40°C; no data are available for

NaCl. 2) In the calculation of the threshold gradient (J-C eq. 53 mentioned above), the values for several parameters are not reliable, as described in previous section. 3) Experimental data by Roedder and Belkin (discussed below) suggesting that no threshold exists.

Because of the importance of the threshold value concept, Roedder and Belkin (unpublished data) have recently extended their laboratory measurements of brine inclusion migration to a much lower thermal gradient, $0.5^{\circ}\text{C cm}^{-1}$, and found that the inclusions still moved at a normalized rate that was $1/3$ that for $1.5^{\circ}\text{C cm}^{-1}$. These two points yield a straightline extrapolation through zero, suggesting that there is no "threshold" gradient value, below which no movement will occur. We realize, of course, that the gradient used in these experiments is still $4\times$ larger than the maximum threshold value of J-C.

Conclusions concerning the rate of migration of fluid inclusions through single salt crystals.

The experimental data needed to verify the brine migration model of Anthony and Cline (1971) are simply not available, especially at higher temperatures ($>50^{\circ}\text{C}$). The maximum migration rates calculated from this model by assuming $K=0$ depend on the composition of brine inclusions, and the estimated values for the parameters D , α , and σ . The Stokes-Einstein relation used to estimate D values is not valid for electrolyte solutions. The method used by J-C for estimating $-\sigma$ values is scientifically unsound, and their estimated ($-\sigma$) values are demonstrably too low. The experimental migration rates reported by Bradshaw and Sanchez (1968, 1969) are too scattered to be used to verify the model, and hence the arbitrary equation (J-C, eq. 42) assumed by Jenks (1979), based on these data, has no theoretical basis. The same is true for applications of this equation, such as in the MIGRAIN-type calculations made by J-C. As the kinetic potentials reported by J-C are also not realistic, the estimations they have made for the upper-bound total volumes of in-migration of H_2O in salt repositories are not reliable.

THE BEHAVIOR OF MIGRATING FLUID INCLUSIONS ON INTERSECTING A GRAIN BOUNDARY

Introduction.

When a thermal gradient is established in a mass of salt crystals containing fluid water, any description of the behavior of this fluid must be discussed in two entirely separate contexts. In the previous section we discussed the migration of water present as fluid inclusions within single crystals of NaCl. However, water is present in salt deposits in several other forms and locations, in addition to the fluid inclusions within single crystals (Roedder and Bassett, 1981).

Intergranular water.

One of the most common forms is as intergranular fluid inclusions, in a spectrum of sizes from the $1\text{-}2\text{ }\mu\text{m}$ inclusions so commonly found on grain boundaries in both domal and bedded salt to the centimeter-sized

vugs between crystals in some bedded salts (Roedder and Belkin, 1977, 1978, 1981; Roedder and Bassett, 1981). Still larger intergranular inclusions, the so called "brine pockets," may be of major importance, but as J-C have specifically excluded them, since they "...will presumably be eliminated by appropriate site selection and repository design" (Abstract, p. 1), we will not deal further with them here. Still another form is as hydrous minerals (particularly clays and hydrated saline minerals). Most such "impurity" phases occur along the grain boundaries between halite crystals. If the temperature becomes high enough at the ambient P_{H_2O} (Jockwer, 1981), these phases may start to break down and add to the amount of free water present along the grain boundaries.

Even if neither intergranular fluid inclusions nor hydrous minerals were present on the grain boundaries at the start, liquid water will be present on the grain boundaries as soon as the first migrating intracrystalline fluid inclusions contact the boundary. In this section, we discuss the fate of intercrystalline fluid on grain boundaries.

"Stopping" of migrating fluid inclusions on intersecting a grain boundary.

In a series of statements, J-C use words which clearly convey the idea that in general, no further movement of fluid will take place once an inclusion contacts a grain boundary (emphasis added):

Executive Summary, pp. xvi-xvii: "Experimental information from the in situ Project Salt Vault experiment showed that most of the brine in bedded salt does not migrate from one crystal into another but instead stops on the boundary between the crystals. Theoretical considerations indicate that large brine inclusions could move across crystal boundaries under a thermal gradient in the salt if they move within the crystal under the same gradient. The experimental observation that most inclusions were stopped on the boundaries might have resulted from the presence of impurities, such as clay and anhydrite, on the boundaries."

Abstract, pp. 1-2: "However, experimental and theoretical data also indicate that most of the brine may not migrate from one crystal into another but instead may be trapped on the boundary between the crystals. Some of this trapping can be explained in terms of differences in energy between an inclusion on a crystal boundary and one within the adjacent crystal. Impurities on the boundary could also be a contributing factor. In any case, it seems likely that extensive trapping on crystal boundaries will occur in the repository salt."

Page 60: "Very few inclusions undergo thermal-gradient-induced migration from one crystal into an adjacent one; they are usually stopped on boundaries between crystals."

Page 67: "Theoretical and experimental information shows that brine inclusions undergoing thermal-gradient-induced migration within crystalline NaCl (and other alkali halides) may either be stopped on a tight crystal boundary or migrate into the adjacent

crystal, depending upon several factors: (1) the size and shape of the inclusion, (2) the presence of impurity solids on the boundary, and (3) the temperature gradient in the salt."

Page 69: "The calculated values listed in Table 9 indicate that brine inclusions for which $X > \sim 0.1$ cm will move across a crystal boundary if they move within the crystal, under the given thermal gradient. Inclusions with smaller values for X might be trapped on a boundary even though they move within the crystal, depending upon several factors including the actual value for γ for NaCl and the prevailing value for ∇T_{∞} ."

Page 73: "Lambert⁷⁷ examined the block after heating and reported on the mineralogical aspect of fluid migration. He found that fluid inclusions within 15 cm of the heater hole had migrated, but rarely across grain boundaries."

Page 74: "Petrofabric examinations of salt samples from a region adjacent to irradiated Array Hole 2 in Project Salt Vault were conducted by Holdaway [sic.]. This region was located in an outward direction from the periphery of the array of waste canisters. Evidence for brine migration within crystals was observed, but only a few trails crossed crystal boundaries. There was some evidence that droplets spread on grain boundaries. These observations appear to support the postulation that brine was trapped on grain boundaries during the heating phases of the Project Salt Vault experiment."

Page 87: "As discussed, it is unlikely that the assumptions regarding continuous brine migration from one crystal into another will be valid for an actual repository in salt. It is much more likely that the brine inclusions will be stopped on crystal boundaries..."

The assumption of such stopping or trapping is based originally on the work of Cline and Anthony (1971) who showed experimentally and theoretically that small inclusions were kept from moving by grain boundaries. But Roedder and Belkin (1977, 1979a) showed that the great bulk of all liquid water present as inclusions in salt was generally present as a few very large inclusions, and these large inclusions, on reaching a boundary, either leaked out or crossed the boundary. Several heater experiments have resulted in migration data that are used by J-C to support their statements. Lambert (1980), in a study of Salt Block II, reported that many larger inclusions migrated "...but stopped, at least 7 centimeters from the heater hole..." Roedder and Belkin (1980b), however, suggested that such apparent "stopping," if not simply a result of the end of the run, represents contact of the inclusion with a grain boundary and subsequent leakage of the contents. Similarly, Holdaway (1974), in a study of the results of the Project Salt Vault experiment, indicated only that the migration trails ended at grain boundaries.

Movement of fluid along grain boundaries.

In contrast to the frequent use of the words "trapped" and "stopped," J-C indicate in various other statements that the fluid is not actually stopped or trapped, but that it can (or will) continue to move on to the emplacement hole, possibly "at some later time" (p. 99), via connected pores and/or microcracks, and they describe several possible mechanisms for movement:

Executive Summary, p. xviii: "Brine on crystal boundaries. Any significant movement of the liquid brine on crystal boundaries into an emplacement hole must take place through connected pores and/or microcracks. Such movement could result from gradients of pressure that could arise in the vapor pressure of H₂O, the radiolytic gas, and/or in the stress state of the salt. Other mechanisms for movement include transport in a thermal gradient analogous to that occurring for brine inclusions within crystals, and capillary action along previously unwetted surfaces. Water vapor, as opposed to liquid brine, could move under gradients of vapor pressure of H₂O and radiolytic gas from a receding liquid front within a microcrack or pore." (Also in Summary and Conclusions, p. 114.)

Abstract, p. 2: "Any significant movement of the brine on crystal boundaries into an emplacement hole will probably take place through connected pores and/or microcracks."

Page 60: "Brine on salt boundaries can move along microcracks or connected pores to the spaces around a waste package. Microcracks could occur along crystal boundaries and/or through crystals."

In addition to the above, J-C assume that such movement does occur, in their estimates of the upper bounds for in-migration:

Executive Summary, p. xx: "Estimates of the upper bounds for in-migration of H₂O to CHLW and SF waste packages in reference repositories from the surrounding salt were made employing the assumption that all of the brine reaching a crystal boundary will reach the emplacement hole at some unspecified later time, presumably by movement through connected pores and microcracks that may develop on the crystal boundary as a result of the collection of brine there."

In spite of the above statement, the "conservative" calculation of J-C of expected brine inflow via MIGRAIN code were made under the assumption that no such movement on pores and/or microcracks occurred (emphasis added):

Executive Summary, p. xix: "The estimated H₂O migration rates during the first 1 to 2 y after emplacement of waste are approximately equal to those calculated by the MIGRAIN code (or by a similar method), assuming 0.5 vol % liquid H₂O (with liquid rates of migration given by the Jenks equation). This assumes

and field. In the laboratory, a piece of core is selected that can be machined into a suitable test piece; the original coring operation and this subsequent selection both tend to bias the sample used away from those local imperfections (shears, fractures, tiny clay seams) that are the normal places for core to break. The irregularities of composition and texture of salt deposits are such that the "avoidance" of "impurity stringers" must be subjective at best, and the more carefully these "stringers" are avoided in laboratory or field, the more unrepresentative and hence geologically unrealistic the resultant data become. Perfectly regular and isotropic rock is very rare, if it exists at all.

Many of the permeability studies that have been made show extremely variable results. Thus J-C report data (their table 8, p. 65) on a series of tests of domal salt from Grand Saline that show initial permeabilities that range over 2 orders of magnitude, and minimum permeabilities ranging over 4 orders of magnitude.

Most important, many of the permeability studies were made with permeation fluids such as kerosene, helium, or argon that were immiscible with the aqueous brines normally in the pores of the salt (e.g., Gloyne and Reynolds, 1961). Surface tension between the two fluids under such conditions can only impede flow, and if the pores are small, can stop it completely. Even when a "saturated" brine is used as the permeation fluid, it is exceedingly difficult to control conditions so rigorously that closure of the pores by precipitation from the permeating fluid itself is not a major source of error. (In this connection, note that declines in permeability with time of up to 3 orders of magnitude were observed in all tests.)

In addition to the above, several lines of evidence seem to contradict the evidence given by J-C of negligible permeability for rock salt in nature. Isotopic and chemical studies of fluids from both brine seeps and fluid inclusions in domal salts suggest an external source for some of these waters (e.g., Knauth et al., 1980; Clynne, M.A., personal communication). Roedder and Belkin (1977, 1978, 1979a) show that salt at the WIPP site has been permeated throughout by fluids of several quite different compositions at various times in the past. No data on flow rates are possible, but the fluids did move, even through massive salt, apparently free of even microscopic "stringers," and under constant "hydrostatic confining pressures."

Conclusions concerning behavior of fluid on grain boundaries.

In view of the uncertainties involved in the behavior of fluids on grain boundaries, and the permeability of the salt, we fail to see how the results of a calculation, made under assumptions that are apparently admitted to be unrealistic, and that apparently agrees with experimental data only "fortuitously," should be considered to be "conservative" (terms as used by J-C).

OVERALL CONCLUSIONS

The conclusions reached by J-C as a result of their calculations of expected brine in-flow to a nuclear waste repository in rock salt are not truly conservative when the observational and theoretical bases are

that all of the liquid is located within crystals and that there are no effects of crystal boundaries on the thermal-gradient-induced migration. Rate values in bedded salt that are estimated in this way are: 250 mL/y and 80 mL/y for packages of CHLW and spent fuel (SF), respectively, and 10 mL/y for a package of defense high-level waste (DHLW).

This method for estimating rates of in-migration was based on observed agreement between experimental values and values calculated as described above. This agreement is probably fortuitous since it is likely that experimentally observed in-migration took place by movement of brine and/or vapor along crystal boundaries as well as by movement of brine inclusions through crystals."

Permeability of salt deposits.

Although no specific rationalization is given by J-C for making a "conservative" calculation under assumptions that appear to be admittedly unrealistic, the rationale seems to lie in the further assumption that salt deposits have exceedingly low permeabilities, as shown by the following quotes from J-C:

Executive Summary, p. xv: "Studies of the permeability of bedded rock salt in the absence of a temperature gradient have been reported by several groups of investigators. There is agreement that undisturbed bedded salt at repository depths has a negligible permeability in the regions which are free of impurity stringers."

Page 60: "The effective permeability of the rock salt walls around a waste package in bedded or domal salt of repository quality, and free of impurity stringers, will be very low: $<5 \text{ fcm}^2$."

Page 61: "There is strong evidence that microcracks within a sample can be healed by application and maintenance of hydrostatic confining pressures comparable to those prevailing in the undisturbed formation."

In response to the last quotation, it has been known for fifty years that in the presence of water, new microcracks within single crystals of salt will heal within seconds in the laboratory, without hydrostatic confining pressures. The crux of the matter lies in the boundaries between different crystals in a polycrystalline rock. These boundaries not only cannot heal into a single crystal individual as above, but are also the usual sites for intercrystalline fluid inclusions and most grains of impurity minerals, as well as being the weakest part, physically, of the rock salt. Most fracture surfaces through rock salt are along grain boundaries.

We believe that most of the permeability measurements of salt discussed by J-C were made under conditions that, for several reasons, are not necessarily applicable to in situ repository conditions, and have yielded permeabilities that are too low. Two types of tests were reported, laboratory

considered. A truly valid calculation is not possible at this time, as there are too many uncertainties, but we suggest that the in-flow calculations of J-C are low, perhaps by several orders of magnitude, as a result of a combination of the following:

1. Assumption of a value of 0.19 wt.% H₂O for bedded salt, whereas the true in situ value is almost certainly much higher, perhaps by a factor of 10 or more.
2. Assumption of a Soret coefficient ($-\sigma$) of 0.004 to 0.005°C⁻¹ between 50° and 200°C, whereas the true value is almost certainly much higher, perhaps even greater than 0.01°C⁻¹.
3. Assumptions about the existence, and magnitude, of a threshold value for the thermal gradient, below which migration is assumed to cease.
4. Assumption that rock salt formations of repository size can be considered to be isotropic and uniformly extremely low in permeability.
5. Assumption that the original location of the water is as intracrystalline inclusions, whereas some and possibly much of the water in any given salt bed is more likely to be already on halite grain boundaries, as intercrystalline fluid inclusions and hydrous mineral impurity grains.
6. Assumption that fluid migration through a polycrystalline, polymineralic rock salt mass can be modelled mathematically as though it were a large single crystal of salt.

We do agree with one recommendation of J-C, that additional in situ experiments of many-year duration are needed, with actual waste emplaced in the salt formation of interest, to establish the long-term brine-migration characteristics for a repository in salt.

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